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Electrical and piezoelectric properties of BiFeO₃ thin films grown on Sr_xCa_{1-x}RuO₃-buffered SrTiO₃ substrates

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(001)-oriented BiFeO₃ (BFO) thin films were grown on Sr_xCa_{1-x}RuO₃- (SCRO; $x = 1, 0.67, 0.33, 0$) buffered SrTiO₃ (001) substrates using pulsed laser deposition. The microstructural, electrical, ferroelectric, and piezoelectric properties of the thin films were considerably affected by the buffer layers. The interface between the BFO films and the SCRO-buffer layer was found to play a dominant role in determining the electrical and piezoelectric behaviors of the films. We found that films grown on SrRuO₃-buffer layers exhibited minimal electrical leakage while films grown on Sr_{0.33}Ca_{0.67}RuO₃-buffer layers had the largest piezoelectric response. The origin of this difference is discussed. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4724332>]

INTRODUCTION

Bismuth ferrite (BiFeO₃) has been extensively studied due to its unique multiferroic properties, which are promising for applications in novel magnetoelectric (ME) devices.^{1,2} Furthermore, promising photovoltaic performances, such as large open-circuit voltage,³ high quantum efficiency,⁴ and appreciable response to visible lights.⁵ Domain walls and interfaces (grain boundaries and ferroelectric-electrode interfaces) are found to play important roles in the photovoltaic effects.^{3,6,7} BFO is ferroelectric (FE) and antiferromagnetic (Anti-FM) in bulk samples, whereas it is FE and ferromagnetic (FM) in thin films and nanoparticles.¹⁻¹⁰ Moreover, the FE Curie temperature and Anti-FM Neel temperature of BFO are 810 °C and 380 °C, respectively, which are high enough for normal applications.^{9,10} The appearance of FM behavior in BFO thin films is related to residual strain, which deforms the crystallographic structure from rhombohedral to tetragonal to some extent.¹ Such deformation suppresses the Anti-FM spiral spin structure and results in the appearance of FM (Ref. 11) and leads to a large electrical remnant polarization ($\sim 130 \mu\text{C}/\text{cm}^2$).^{1,12} Recently, a substantial piezoelectric response ($\sim 5\%$) was observed in BFO films with coexistence of tetragonal and rhombohedral crystal structures.¹³ Additionally, transitions between the tetragonal phase and the rhombohedral phase can be controlled by external electrical field¹⁴ and a new temperature-induced phase transitions around 100 °C was recently observed in these highly strained BFO films.¹⁵ It seems clear, then that strain considerably affects the magnetic, electrical and piezoelectric behaviors of BFO films. Here, we report on how the introduction of different strain states affects BFO thin films grown on different substrates. To this end, we chose Sr_xCa_{1-x}RuO₃- (SCRO; $x = 1, 0.67, 0.33, 0$) buffered SrTiO₃ (001) crystals as the substrates. SCRO is highly conductive and is often used as the bottom

electrode in electrical characterizations.^{1,12-14,16,17} The lattice constants of pseudo-cubic SCRO are 3.92 Å, 3.89 Å, 3.87 Å, and 3.84 Å, for $x = 1, 0.67, 0.33$, and 0, respectively (as shown below). The lattice constant of bulk BFO is 3.96 Å, which is clearly larger than that of SCRO. Therefore, the expected lattice mismatch would be 1.1%, 1.9%, 2.3%, and 3.0%, respectively. In addition, the expected stress state would be compressive. Although previous work used thin SrRuO₃-buffered layers (10–80 nm thick) as the bottom electrode in BFO films and varied the strain state by using different substrates, such as SrTiO₃, LaAlO₃, YAlO₃, and Pt,¹⁸⁻²¹ the effects of conductive buffer layers on the performance of BFO thin films has not yet been studied systematically.

EXPERIMENTAL

SCRO and BFO targets were synthesized using the conventional solid-state reaction technique. BiFeO₃ ceramics were prepared from reagent-grade Bi₂O₃ and Fe₂O₃ powders (Sigma-Aldrich). The raw materials were well mixed by ball-milling, pressed into 1-in.-diameter disks under a uniaxial pressure of 200 MPa, and then sintered at 795 °C for 30 min. Excess Bi was added to compensate for the loss of Bi during processing. The Sr_xCa_{1-x}RuO₃ targets were prepared using SrCO₃, CaCO₃, and RuO₂ raw powders, which were sintered at 1500 °C for 4 h. The target composition and crystal structure were confirmed by x-ray fluorescence (XRF) and x-ray diffraction (XRD) patterns.

The SCRO-buffer layers and BFO films were successively deposited onto SrTiO₃ (001) single-crystal substrates using pulsed laser deposition (PLD). During deposition, the substrate temperature was fixed at 750 °C for SCRO and 650 °C for BFO, and the oxygen pressure was kept at 150 mTorr for both layers. The thicknesses of the SCRO layers and BFO layers were both around 380 nm. The laser (KrF, 248 nm) was operated at 5 Hz with an energy density of 7 J/cm² at the target surface. The distance between the target and substrate was 4 cm. After deposition, 400 Torr of oxygen was

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introduced into the chamber and the sample was annealed at 650 °C for 20 min under this oxygen environment. Au electrodes of that were 20 nm thick and 0.2 mm in diameter were sputtered onto the BFO films. The crystal structure of the samples was characterized by an x-ray diffractometer (XRD, Bruker D8 Discover). The surface morphology and piezoelectric response were characterized by atomic force microscopy (AFM, Agilent 5400). Electrical leakage currents and ferroelectric polarization were measured using a ferroelectric tester (aixACCT).

RESULTS AND DISCUSSION

The XRD patterns of the BFO thin films and the SCRO-buffer layers are shown in Figure 1. The SCRO-buffer layers were well crystallized and oriented in the (001) direction. The BFO films grown on SrRuO_3 - and $\text{Sr}_{0.67}\text{Ca}_{0.33}\text{RuO}_3$ -buffered substrates exhibited only (001) orientations. In the BFO films grown on $\text{Sr}_{0.33}\text{Ca}_{0.67}\text{RuO}_3$ - and CaRuO_3 -buffered substrates, a weak (110) peak, around 10% of the intensity of the major (001) peak, also appeared, as shown in Figure 1(a). The larger lattice mismatch between the BFO films and these two buffered layers is the likely reason for this difference. In all the films, tiny amounts of secondary-phase $\text{Bi}_{25}\text{FeO}_{40}$ and

$\text{Bi}_2\text{Fe}_4\text{O}_9$ were detected. Decomposition of the BFO film during high-temperature processing could be the origin of the phase impurities.^{22–24} Enlarged views of the (001) peaks are shown in Figures 1(c) and 1(d) for BFO films and the buffer layers, respectively. The (001) diffraction positions (2θ) of the buffer layers were 22.51°, 22.58°, 22.63°, and 23.12°, for SrRuO_3 , $\text{Sr}_{0.67}\text{Ca}_{0.33}\text{RuO}_3$, $\text{Sr}_{0.33}\text{Ca}_{0.67}\text{RuO}_3$, and CaRuO_3 , respectively. The corresponding bulk values were 22.68°, 22.86°, 22.96°, and 23.13°, as shown in the inset of Figure 1(d). Low shifts of XRD peak positions (or increase of lattice constant) were present in all buffer layers, indicating tensile stress in the SCRO layers. In the BFO films, the (001) peak positions were 22.42°, 22.44°, 22.48°, and 22.50°, for buffer layers of SrRuO_3 , $\text{Sr}_{0.67}\text{Ca}_{0.33}\text{RuO}_3$, $\text{Sr}_{0.33}\text{Ca}_{0.67}\text{RuO}_3$, and CaRuO_3 , respectively. Meanwhile, the BFO target had its (001) peak at 22.40°. In comparison with its bulk value, the lattice constant of BFO film decreased gradually with different SCRO buffer layers from SrRuO_3 to CaRuO_3 . Therefore, the stress state (compressive) of the BFO films increased gradually as the buffer layer changed from SrRuO_3 to CaRuO_3 .

AFM images showing the surface microstructures of the BFO films are presented in Figure 2. All the samples are dense, uniform with no large pores. The grain sizes were

FIG. 1. XRD patterns of (a) BFO thin films on $\text{Sr}_x\text{Ca}_{1-x}\text{RuO}_3$ -buffered SrTiO_3 substrates, (b) bare $\text{Sr}_x\text{Ca}_{1-x}\text{RuO}_3$ -buffered SrTiO_3 substrates, and enlarged view of the pseudo-cubic (001) diffraction peaks of (c) BFO thin films and (d) $\text{Sr}_x\text{Ca}_{1-x}\text{RuO}_3$ -buffer layers. Inset in (d) shows the (001) diffraction peaks of bulk $\text{Sr}_x\text{Ca}_{1-x}\text{RuO}_3$ ceramics. The dotted lines are guides.

FIG. 2. AFM images of (a) BFO-SrRuO₃, (b) BFO-Sr_{0.67}Ca_{0.33}RuO₃, (c) BFO-Sr_{0.33}Ca_{0.67}RuO₃, and (d) BFO-CaRuO₃.

260 nm, 207 nm, 186 nm, and 134 nm in films with SrRuO₃, Sr_{0.67}Ca_{0.33}RuO₃, Sr_{0.33}Ca_{0.67}RuO₃, and CaRuO₃-buffer layers, respectively. The corresponding surface roughness (R_a) values were 15.8 nm, 14.6 nm, 12.1 nm, and 7.0 nm, respectively. The BFO film grown on the SrRuO₃-buffered layer had the largest grain size and also the most rough surface, while the smallest grain size and the smoothest surface were found in the film with the CaRuO₃-buffer layer. The smaller grains, or more grain boundaries, observed in the BFO on the CaRuO₃-buffer layer can be understood in terms of film energy.²⁵ In largely strained and thick films (thicker than tens of nanometers), grain boundaries are energetically favorable to reduce the strain energy. This will result in smaller grains. Another possible reason for the difference in BFO grain sizes may be associated with the microstructures of the underlying buffered layers, which are shown in Figure 3. The roughness values (R_a) were 1.79 nm, 0.52 nm, 0.65 nm, and 1.30 nm for SrRuO₃, Sr_{0.67}Ca_{0.33}RuO₃, Sr_{0.33}Ca_{0.67}RuO₃, and CaRuO₃, respectively. Different microstructures, such as step-like (SrRuO₃, Sr_{0.33}Ca_{0.67}RuO₃) and spiral-like (Sr_{0.67}Ca_{0.33}RuO₃), were observed. More importantly, the

grain sizes varied significantly in different buffer layers (larger in SrRuO₃, Sr_{0.67}Ca_{0.33}RuO₃ and smaller in Sr_{0.67}Ca_{0.33}RuO₃, CaRuO₃) and the larger grain sizes in the buffer layers could facilitate BFO film growth.

Figure 4 shows the I-V curves of the BFO films. The measurement setup is shown in the inset to Figure 4(a). The leakage currents in the BFO film on SrRuO₃ are much smaller than those with other buffer layers. At the maximum electrical field (8 V–210 kV/cm), the leakage current in the film on the SrRuO₃-buffer layer was $1.02 \times 10^3 \mu\text{A}/\text{cm}^2$, while for the film on the Sr_{0.33}Ca_{0.67}RuO₃-buffer layer was $\sim 27.2 \times 10^3 \mu\text{A}/\text{cm}^2$. The maximum leakage currents in different samples are summarized in the inset to Figure 4(c). The polarization reversal currents ($\sim 10 \mu\text{A}/\text{cm}^2$) contributed little to the measured leakage currents (10^3 – $10^4 \mu\text{A}/\text{cm}^2$). Their effects can be excluded. The sheet resistances of the underlying buffer layers were 9 $\Omega/\square$, 19 $\Omega/\square$, 12 $\Omega/\square$, and 35 $\Omega/\square$ for SrRuO₃, Sr_{0.67}Ca_{0.33}RuO₃, Sr_{0.33}Ca_{0.67}RuO₃, and CaRuO₃, respectively. The values are comparable with the published data.²⁶ The resistance of the CaRuO₃-buffer layer is much larger than the resistance of the other buffer layers,

FIG. 3. AFM images of buffer layers (a) SrRuO_3 , (b) $\text{Sr}_{0.67}\text{Ca}_{0.33}\text{RuO}_3$, (c) $\text{Sr}_{0.33}\text{Ca}_{0.67}\text{RuO}_3$, and (d) CaRuO_3 .

which could affect the I-V behaviors of the BFO films. Such effects need further investigations.

The most interesting feature of these I-V curves is the highly asymmetric or diode-like I-V behaviors observed in the films grown on SrRuO_3 , $\text{Sr}_{0.67}\text{Ca}_{0.33}\text{RuO}_3$, and $\text{Sr}_{0.33}\text{Ca}_{0.67}\text{RuO}_3$ -buffer layers. However, the I-V curves for the film grown on the CaRuO_3 -buffer layer under positive or negative electrical bias are almost symmetric. Such asymmetric I-V characteristics have been observed in many metal-ferroelectric-metal and metal-ferroelectric-semiconductor-metal configurations.^{27–36} Different top and bottom electrodes may be the origin of these highly asymmetric I-V behaviors, as previously demonstrated in Au-BFO-ZnO,²⁹ Pt-BaTiO₃-ZnO,²⁸ Au-(Pb,Lu)(Zr,Ti)O₃-SrTiO₃:Nb,³⁶ Pt-BFO-SRO

(Refs. 37 and 38) heterostructures. In current configurations, i.e., Au-BFO-SCRO, these different bottom and top electrodes can also lead to highly asymmetric I-V behaviors, as two p-n junctions connected back-to-back (as discussed below).

Another intriguing point is the nonconformity of the leakage currents during field-increasing or “forward sweep” and field-decreasing or “reverse sweep” (hysteresis behavior). The nonconformity is considered to be related to ferroelectric polarization states.³⁹ Some reports on resistance switching and rectifying diode effects in ferroelectric capacitors suggest that the resistivity of the metal/ferroelectric/metal structure is indeed affected by the polarization states.^{32,37–41} In BFO films, it was found that the BFO-electrode interface barrier could be changed (increased or decreased) by the ferroelectric

FIG. 4. Leakage currents in BFO thin films on different buffer layers of (a) SrRuO_3 , (b) $\text{Sr}_{0.67}\text{Ca}_{0.33}\text{RuO}_3$, (c) $\text{Sr}_{0.33}\text{Ca}_{0.67}\text{RuO}_3$, and (d) CaRuO_3 . The measurement step is 0.2 V with a delay time of 2 s. The inset in (a) illustrates the I-V measurement configurations. Inset in (c) shows the maximum leakage current at +8 V of all films on different buffer layers.

polarization through the effects of polarization charges.^{38,41} The conduction in BFO films was considered to be p-type, which was induced by Bi-loss (like acceptor doping) during film formation at high temperature.⁴¹ Under positive bias, the interface between BFO and the bottom SCRO electrode is in the “non-blocking” state (like a forward-biased p-n junction), while the interface between BFO and the top Au electrode is in the “blocking” state (like a reverse-biased p-n junction). Therefore, the leakage current in a SCRO-BFO-Au structure is dominated by the “blocking” BFO-Au interface. Similarly, under negative bias, the leakage is governed by the BFO-SCRO interface. Considering that the polarization state under positive bias, during forward sweep ($0 \text{ V} \rightarrow +8 \text{ V}$), the polarization is initially upwards (pointing to top electrode, defined as “-P”) and then switches to downwards (pointing to bottom electrode, defined as “+P”) as the applied voltage exceeding a certain point (V_c), and stays downwards (+P) during the reverse sweep ($+8 \text{ V} \rightarrow 0$). Moreover, for downwards polarization (+P), the polarization during field-decreasing ($+8 \text{ V} \rightarrow V_c$) is larger than that during field-increasing ($V_c \rightarrow +8 \text{ V}$) (this holds for a real ferroelectric capacitor; for an ideal one, they are equal). When the polarization direction is -P, positive polarization charges accumulate at the BFO-Au interface, which will increase the potential barrier for the charge carrier (hole) injection from the Au electrode (“repel holes”). When the polarization switches to +P, negative polarization charges appear at the BFO-Au interface, which will then lower the potential barrier (“attract holes”). The +P polarization is larger under reverse sweep as stated above, and the potential barrier will be lower. Therefore, the leakage current is larger during the reverse sweep due to the lower interface barrier. The band diagrams under a positive bias with -P and +P are shown in Figures 5(a) and 5(b), respectively. The built-in potential barrier can thus be changed by the ferroelectric polarization by,^{38,41}

$$\Delta\phi_{bi} = \frac{\pm p\delta}{\epsilon_0\epsilon_s}, \quad (1)$$

where P is the ferroelectric polarization, δ is the thickness of the interface layer between the surface polarization charge and the electrode, ϵ_0 is the vacuum permittivity, and ϵ_s is the static dielectric constant of the film. Wang *et al.* obtained a $\Delta\phi_{bi}$ of 1.38 eV using $P = 60 \mu\text{C}/\text{cm}^2$, $\delta = 1 \text{ nm}$, $\epsilon_s = 50$, for a 240 nm BFO film in a Pt-BFO-SRO structure prepared by PLD,³⁷ while Lee *et al.* calculated $\Delta\phi_{bi}$ to be 0.6 eV using $P = 65 \mu\text{C}/\text{cm}^2$, $\delta = 1 \text{ nm}$, $\epsilon_s = 100$, for a 400 nm BFO film in a Pt-BFO-SRO structure deposited by sputtering.³⁸ In our case, P is only $15.5 \mu\text{C}/\text{cm}^2$ for the Au-BFO-SRO sample. The change in the potential barrier would therefore be expected to be 0.1–0.4 eV. The potential barrier height without charges at the interface is expected to be $\sim 0.6 \text{ eV}$, which depends on the density of impurities in the film, especially around the interface region.⁴¹ Next, we consider the case of negative biases, where the interface between BFO and Au is “non-blocking” and that between BFO and SCRO is “blocking.” In the same way, the leakage current during forward sweep ($0 \rightarrow -8 \text{ V}$) is lower than that during reverse sweep ($-8 \text{ V} \rightarrow 0$). However, compared with the case of positive biases, suppressed hysteresis and much lower leakage currents are observed, which indicates a higher potential barrier at the BFO-SCRO interface under negative bias than that at the BFO-Au interface under positive bias. The higher barrier may be induced by the accumulated positively charged oxygen vacancies (V_o) at the BFO-SCRO interface due to the self-poled upwards polarization (parallel with -P): a negative polarization charge is built up near the bottom SCRO electrode, which attracts V_o to migrate towards the SCRO electrode at high temperatures during deposition.⁴¹ A rough interface may facilitate the accumulation of these oxygen vacancies. The roughness of the SRO bottom

FIG. 5. Band diagrams for the BFO-Au interface under positive (a) forward, (b) reverse bias and the BFO-SCRO interface under negative (c) forward, and (d) reverse bias. The applied field (positive or negative) is at the top Au electrode. E_F : Fermi level, VB: valence band, V_o : positively charged oxygen vacancies, ϕ_{bi-Au}^{+P} : built-in potential barrier at the BFO-Au interface with the ferroelectric polarization inside the film pointing to the top Au electrode (-P), ϕ_{bi-Au}^{-P} : built-in potential barrier at the BFO-Au interface with the ferroelectric polarization inside the film pointing to the bottom SCRO electrode (+P), $\phi_{bi-SCRO}^{+P}$: built-in potential barrier at the BFO-SCRO interface with the ferroelectric polarization inside the film pointing to the top Au electrode (-P), $\phi_{bi-SCRO}^{-P}$: built-in potential barrier at the BFO-SCRO interface with the ferroelectric polarization inside the film pointing to the bottom SCRO electrode (+P).

FIG. 6. Fitting results for the leakage currents in BFO films on the $\text{Sr}_{0.33}\text{Ca}_{0.67}\text{RuO}_3$ -buffer layers under (a) positive and (b) negative bias. “TFL” indicates the onset of the traps-filled-level.

electrode (1.79 nm) is the greatest among all the SCRO electrodes and the film on the SRO electrodes exhibits the most striking asymmetric I-V behavior. These localized permanent positive charges lead to the formation of a high potential barrier at the SCRO-BFO interface for the positive charge carriers (holes), as shown in Figures 5(c) and 5(d). The barrier height is so large that it overtakes the effects of the ferroelectric polarization charges. Therefore, the leakage current under negative bias is much smaller and the hysteresis is also not that exaggerated. This scenario also accounts for the asymmetric I-V behaviors.

Several types of leakage or conduction mechanisms may contribute the leakage current, including Ohmic conduction, space-charge-limited-conduction (SCLC), interface-limited Schottky emission, bulk-limited Poole-Frenkel (PF) emission, interface-limited Fowler-Nordheim (FN) tunneling, and hopping conduction (HC).^{27–35} These mechanisms can be described by the following equations,

$$J_{\text{SCLC}} = \frac{9\mu\epsilon_0\epsilon_r}{8d} E^n, \quad (2)$$

where d is the film thickness, μ is the charge carrier mobility, ϵ_0 is the vacuum permittivity, ϵ_r is the relative dielectric constant of the film, E is the electrical field, J is the current density, $n = 2$ for trap-free conditions, $n > 2$ for SCLC with charge carrier traps;

$$J_{\text{Schottky}} = AT^2 e^{\frac{-\phi - \sqrt{qE/\pi\epsilon_0 K}}{k_B T}}, \quad (3)$$

where A is constant, ϕ is the Schottky barrier, T is the absolute temperature in Kelvin, q is the elemental charge, K is the optical dielectric permittivity ($K \sim 6.25$ for BFO), k_B is the Boltzmann constant;

$$J_{\text{PF}} = BE e^{\frac{-E_1 - \sqrt{qE/\pi\epsilon_0 K}}{k_B T}}, \quad (4)$$

where B is constant and E_1 is the trap ionization energy;

$$J_{\text{FN}} = CE^2 e^{\frac{-D^2 \sqrt{\phi_i}}{E}}, \quad (5)$$

where C and D are constants and ϕ_i is the potential barrier height;

$$J_{\text{Hopping}} = qanv e^{\frac{qaE}{k_B T} - \frac{E_a}{k_B T}}, \quad (6)$$

where a is the average hopping distance, n is the charge carrier density, v is the frequency of the thermal vibration of the electrons at the trap sites, and E_a is the activation energy of trapped charges.

By fitting the experimental data in the coordinates of $\ln(J)$ vs. $\ln(E)$ (SCLC or Ohmic), J/T^2 vs. $E^{0.5}$ (Schottky), J/E vs. $E^{0.5}$ (PF), J/E^2 vs. E^{-1} (FN), and $\ln(J)$ vs. E (Hopping), it is possible to determine which mechanisms contribute to the leakage currents. In all BFO films, SCLC dominated the leakage currents under a high electrical field and Ohmic conduction under a low electric field. The conduction mechanisms under a negative bias resembled those under a positive bias. The slope (n) of the $\ln(J)$ - $\ln(E)$ plot in the SCLC region was found to be 1.7–3.0, deviating from the ideal value of 2. This is related to the distribution of the charge carrier traps in the bandgap, which depends on the applied field.³⁴ One example of these fittings is shown in Figure 6 for the BFO on $\text{Sr}_{0.33}\text{Ca}_{0.67}\text{RuO}_3$. The filled traps level was also observed, where n was much larger than 2 (6.4 and 5.5 as shown in Figure 6). The physical nature of the charge carrier traps is believed to be the structural defects or impurities, for example the cation/anion vacancies.⁴²

The ferroelectric hysteresis loops of the films are shown in Figure 7. All films exhibited well-defined loops. However, the films grown on $\text{Sr}_{0.33}\text{Ca}_{0.67}\text{RuO}_3$ -buffer layer exhibited a rounded shape, indicating considerable contribution from leakage currents. The remnant polarization (P_r) and coercive field (E_c) in the film on the SrRuO_3 -buffer layer are $15.5 \mu\text{C}/\text{cm}^2$ and $176 \text{ kV}/\text{cm}$, respectively.

FIG. 7. Ferroelectric hysteresis loops of BFO thin films on $\text{Sr}_x\text{Ca}_{1-x}\text{RuO}_3$ -buffered SrTiO_3 substrates.

FIG. 8. PFM images (phase) of (a) BFO-SrRuO₃, (b) BFO-Sr_{0.67}Ca_{0.33}RuO₃, (c) BFO-Sr_{0.33}Ca_{0.67}RuO₃, and (d) BFO-CaRuO₃.

The small P_r , compared with other BFO films (~ 50 – $130 \mu\text{C}/\text{cm}^2$ (Refs. 1, 5, 6, and 9)), may be due to the secondary phase or smaller grain size in our samples, as shown in Figure 1(a).

The piezoelectric responses of the films are shown in Figures 8 and 9. Figure 8 shows the piezoelectric force microscopy (PFM) phase pictures of non-poled films. Large ferroelectric domains are clearly observed in the BFO films

FIG. 9. Local piezo-responses, amplitudes (black solid circles) and phases (blue solid lines), of (a) BFO-SrRuO₃, (b) BFO-Sr_{0.67}Ca_{0.33}RuO₃, (c) BFO-Sr_{0.33}Ca_{0.67}RuO₃, and (d) BFO-CaRuO₃.

grown on SrRuO₃ and Sr_{0.67}Ca_{0.33}RuO₃-buffer layers. The domain sizes are much smaller and the contrast between different domains is blurred in these two samples. Two factors may account for these differences: the film orientation and grain size. As shown previously, the films grown on SrRuO₃ and Sr_{0.67}Ca_{0.33}RuO₃-buffer layers are highly (001) oriented and exhibit larger grain sizes (260 nm and 207 nm). The (110) orientation was observed in the other two samples, even at a low percentage and the grain sizes are also smaller (186 nm and 134 nm). However, the piezo-response (amplitude) is the largest in the film grown on the Sr_{0.33}Ca_{0.67}RuO₃-buffer layer, which is 0.233 V under an applied field of 10 V. The corresponding values for the films on SrRuO₃, Sr_{0.67}Ca_{0.33}RuO₃, and CaRuO₃-buffer layers are 0.167 V, 0.184 V, and 0.172 V, respectively, as shown in Figure 8. Another interesting point observed in Figure 9 is the smaller local coercive fields in the sample grown on Sr_{0.33}Ca_{0.67}RuO₃ and CaRuO₃-buffer layers, which are 0.49 V and 0.40 V compared with 0.62 V in BFO-SrRuO₃ and 1.21 V in BFO-Sr_{0.67}Ca_{0.33}RuO₃. This difference may be related to the larger lattice-mismatch strains in the films on Sr_{0.33}Ca_{0.67}RuO₃ and CaRuO₃ buffer layers, as discussed previously. The large strain will deform the crystal structure of BFO from rhombohedral to tetragonal to some extent and then improve the piezoelectric (d_{33}) and ferroelectric (P_r and E_c) properties.^{12,13,19} In our case, the structural differences cannot be determined as their XRD diffraction peaks are overshadowed by the buffer layers. But the lattice constants of the films with different buffer layers are indeed different, as shown in the XRD results. Therefore, we may expect lattice deformation in films with larger strains and therefore enhanced piezoelectric performance. The final point worth mentioning is the much smaller coercive fields (0.40–1.21 V) measured by local PFM compared with those (6.69–12.49 V, see Figure 7) obtained from the ferroelectric hysteresis measurements. The origin for this may be (1) the smaller electrode area (~ 20 nm in diameter) of the PFM tip, which could induce enhancement of a localized electrical field due to the sharpness of the tip and the tip-contact geometry²⁷ and (2) the non-ferroelectric secondary phases (as shown in Figure 1(a)), which will hinder the polarization reversal in larger area (2×10^5 nm in diameter) measurements and may not manifest itself in the local (20 nm in diameter) PFM measurements.

CONCLUSIONS

Effects of buffer layers (SrRuO₃, Sr_{0.67}Ca_{0.33}RuO₃, Sr_{0.33}Ca_{0.67}RuO₃, CaRuO₃) on the microstructural, crystallographic, electrical, ferroelectric, and piezoelectric properties of (001)-oriented BFO thin films were systematically studied. It was found that the lattice constants of the BFO films changed gradually as the buffer layer was varied from SrRuO₃ to CaRuO₃. Diode behavior in the I-V curves was observed in the BFO films on SrRuO₃, Sr_{0.67}Ca_{0.33}RuO₃, Sr_{0.33}Ca_{0.67}RuO₃-buffered layers. Space-charge-limited-conduction mechanism was verified in the leakage of all the films. The film on SrRuO₃ exhibited the lowest leakage current and a well-saturated ferroelectric hysteresis loop. Different piezoelectric responses, revealed by PFM method, were

observed in these films. BFO films with large strains showed increased piezo responses. Different strain states in these films may account for these observations.

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